

High-Temperature Properties of Piezoelectric Langatate Single Crystals

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ABSTRACT : Langasite type crystals belong to non-polar point group of 32 and do not show any phase transformations up to the melting temperature. Langatate ($\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$) demonstrates piezoelectric activity better than quartz and possesses attractive properties for high temperature sensors, resonators and filter applications. High-quality and colorless langatate crystals were grown by the Czochralski technique. The electromechanical and electrical properties of langatate crystals in different crystallographic directions were characterized at elevated temperature. The piezoelectric coefficient along x-axis was 7 pC/N as measured by a Berlincourt meter for a plate geometry with an aspect ratio of 10:1. The dielectric constant did not exhibit any significant temperature dependence ($K_{33} \approx 21$ at 30 °C and $K_{33} \approx 23$ at 600 °C). Loss tangent at 100 kHz remained <0.003 up to 300 °C and <0.65 at 600 °C. The dielectric properties along the y-axis were similar and its temperature dependence was analogous to the x-axis. Electromechanically, the inactive z-axis exhibited no resonance with $K_{33} \approx 84$ at room temperature, decreasing down to ≈ 49 at 600 °C. Resistivity of these crystals along x-axis decreased from $\approx 6 \times 10^{11} \Omega\text{-cm}$ at room temperature, to $\approx 1.6 \times 10^{16} \Omega\text{-cm}$ at 600 °C.

Keywords : Piezoelectric, langatate, langasite, high temperature, dielectric

1. INTRODUCTION:

Langatate ($\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$) single crystals, like langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$), belong to the trigonal point group 32.¹ These piezoelectric crystals show no phase transformation up to their melting temperature ($>1400^\circ\text{C}$)², and possess attractive properties for high temperature applications such as sensors, resonators and filters.¹⁻⁴ Langatate has demonstrated a Qf (Q=quality factor, f=frequency) product superior to quartz. The highest Qf is expected from low defect (dislocation) density crystals. In addition they are non-polar, making the device design easier due to the absence of pyroelectric charge. Langasite type crystals have shown to be superior to quartz, which belongs to the same point group, in resonator applications.⁵ However, their potential for piezoelectric applications such as pressure sensors has not been fully investigated. We investigated the electrical and electromechanical properties of the langatate single crystals with different crystallographic directions as a function of temperature up to 600 °C.

2. CRYSTAL GROWTH:

The performance of langatate crystals are strongly related to the quality of the crystals for the reason that first order material constants (stiffness, piezoelectric coefficient and permeability) and quasi-static frequency-temperature characteristics (nonlinear properties) are linked to defects. The physical properties and target use potential strongly relies on the processing of good quality crystals. Langatate

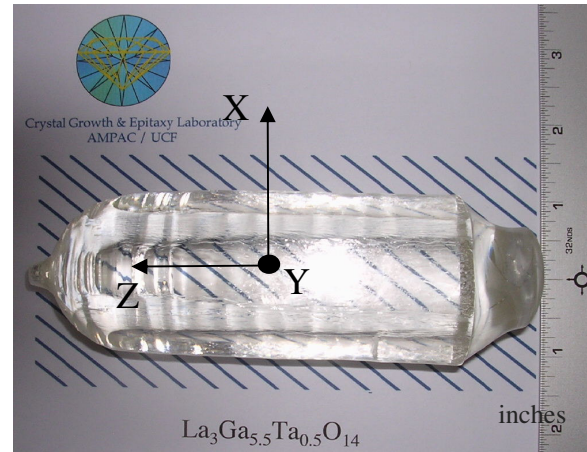


Figure 1: Langatate single crystals grown at UCF.

crystals were grown at University of Central Florida (UCF) Crystal Growth and Epitaxy Laboratory using the Czochralski technique with aim to minimize the defects (Figure 1).

Charge compositions were prepared to take into account of the potential chemical reaction of La_2O_3 with water. The La_2O_3 powder was baked at 800 °C for 12 hrs before weighing and an extra amount of Ga_2O_3 was added to compensate for volatilization. The langatate crystals were grown at UCF using a 50kW Czochralski apparatus

(Pillar Industries) using iridium metal crucibles and a 1 to 3 mm/h pull-rate (rotation rate 10- to 30 rpm). Process control software that was developed specifically for the growth of the langasite family of crystals, utilized a double-loop proportional PID system to take into account both output power and growth rate of the crystal. This approach provided a pathway for a high degree of diameter control and minimized the formation of striations. To minimize the point defect formation and eliminate the color center, a specified partial pressure of oxygen was maintained by adjusting the flow rate of nitrogen. In addition, the crystals were annealed in situ at around 1350 °C for 15 h to release thermal stresses. The relationship between faceting and crystal imperfections such as striations, dislocations, and inclusions has been published previously.⁶

3. ELECTRICAL PROPERTIES:

The principal orientations were named x, y and z in accordance with orthogonal space and measurement axes. The x- and z-measurement axes correspond to their crystallographic equivalents. The y measurement axis was 30° off the crystallographic y-axis. Crystallographic y-axis is 120° to the x-axis in the xy-plane and is equivalent to it due to the 3-fold rotation along the z-axis.⁷ In the rest of this paper the orientations x,y and z refer to the measurement axes.

Dielectric constant measurements were carried out by using an impedance analyzer (Agilent 4294A). Measurements were conducted at high temperatures using a custom furnace and an Agilent 16334A type connector. Data were automatically collected by a LabView (National Instruments Corp.) program. Additional impedance spectroscopy measurements, including low frequency range (>1Hz), were carried out using a Solartron SI1260 Impedance analyzer as a function of temperature. The impedance spectroscopy data was analyzed using Z-view (Scribener Associates Inc.) software. Piezoelectric constant measurements were carried out by a Berlincourt type d_{33} -meter (KCF Technologies) and polarization loops were measured using a ferroelectric analyzer (Radiant Technologies).

The piezoelectric coefficient (d_{33}) was 7 pC/N along the x-axis as measured by the Berlincourt meter. No piezoelectric activity was observed along the y- and z-axis using the Berlincourt meter. The resonance and antiresonance analysis with low DC bias showed the main resonance and anti-resonance peaks along the x-axis were around 227 kHz and 232 kHz, respectively. The effective electromechanical coefficient (k_{eff}) was 0.21 at room temperature along this direction. The temperature dependence of k_{eff} is given in Figure 2. Along the y-axis a clean single mode was detected with resonance and anti-resonance peaks around 250 kHz and 251 kHz, respectively. There was no resonance peaks measured by Agilent 4294A along the z-axis.

The weak-field dielectric constant measured along x- and y-axis did not show any significant dependence on temperature (K_{33} = 21 and 27 at room temperature and K_{33} = 23 and 31 at 600 °C for x- and y-axes, respectively). However, the weak-field dielectric constant was much higher (K_{33} = 84 at room temperature) along z-axis and had

a greater temperature dependence (Figure 3). The loss tangent, $\tan \delta$, at 100 kHz was very small at room temperature (Table 1) along all three axes. At higher temperatures (>350 °C), $\tan \delta$ started to increase, however at 500 °C it was still <0.17 and at 600 °C, <1.

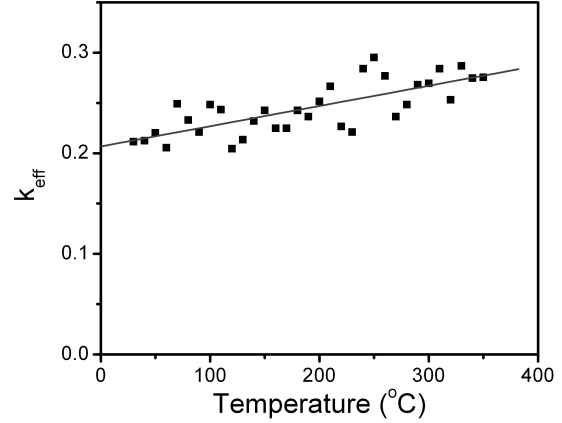


Figure 2: Effective electromechanical coefficient as a function of temperature along x-axis of langatate single crystals. Solid line represents the best fit.

Table I: Room temperature dielectric and electromechanical properties of langatate single crystal along principal orthogonal axes.

	K_{33} (at 30 °C)	$\tan \delta$ (at 30 °C)	d_{33} (pC/N) (at 25 °C)
X-axis	21	0.002	7
Y-axis	27	0.003	0
Z-axis	84	0.017	0

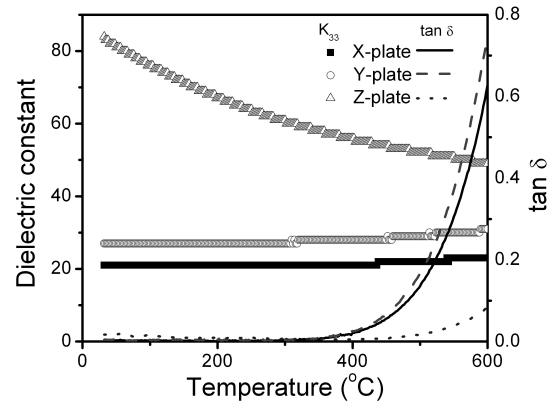


Figure 3: Dielectric constant and loss tangent as a function of temperature along x-, y- and z- axes of langatate single crystals.

Field induced polarization exhibited linear behavior (Figure 4). While measurements up to 10 kV/cm along x-axis have shown no width to the polarization loops at 50 °C and 150 °C, the loops started to widen at 250 °C due to increased losses. However, this width was still too small to characterize the crystal as “lossy”. The high field dielectric

constant can be calculated from the slope of the polarization loops by utilizing the relationship:

$$P = \epsilon_0 (K - 1)E ,$$

where P , ϵ_0 , K , and E are polarization, permittivity of the free space, dielectric constant and electric field, respectively. The high-field dielectric constant that was calculated from the slope of polarization loops was 54 and did not change for any of the temperatures measured up to 250 °C.

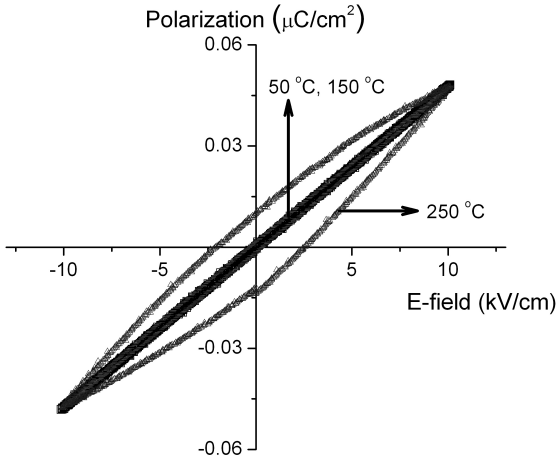


Figure 4: Field induced polarization along the x-axis at temperatures 50, 150 and 250 °C

Impedance spectroscopy analysis of langatate single crystals revealed single arcs from 1 Hz to 1 MHz as a function of temperature up to 600 °C. This manifests a response of single crystals without any grain boundaries. An example of such measurements is given in Figure 5. A single equivalent circuit with a parallel resistor (representing the leakage) and a parallel constant phase element was fitted using the Z-view software. The impedance spectroscopy analysis (Fig. 5), temperature dependent dielectric constant and loss tangent data, as a function of temperature, is indicative of the high quality of the crystal.

The resistivity values calculated from the impedance spectroscopy analysis has been plotted in Fig. 6. Applying an Arrhenius type equation:

$$\sigma \propto \exp\left(\frac{E_{ac}}{kT}\right),$$

where σ , E_{ac} , k and T are conductivity, activation energy, Boltzmann constant and temperature, respectively, allows calculation of activation energies of the conducting species in the langatate single crystals as a function of orientation.

The activation energies calculated from these plots were 0.35, 0.43 and 0.35 eV along x-, y- and z-axes, respectively.

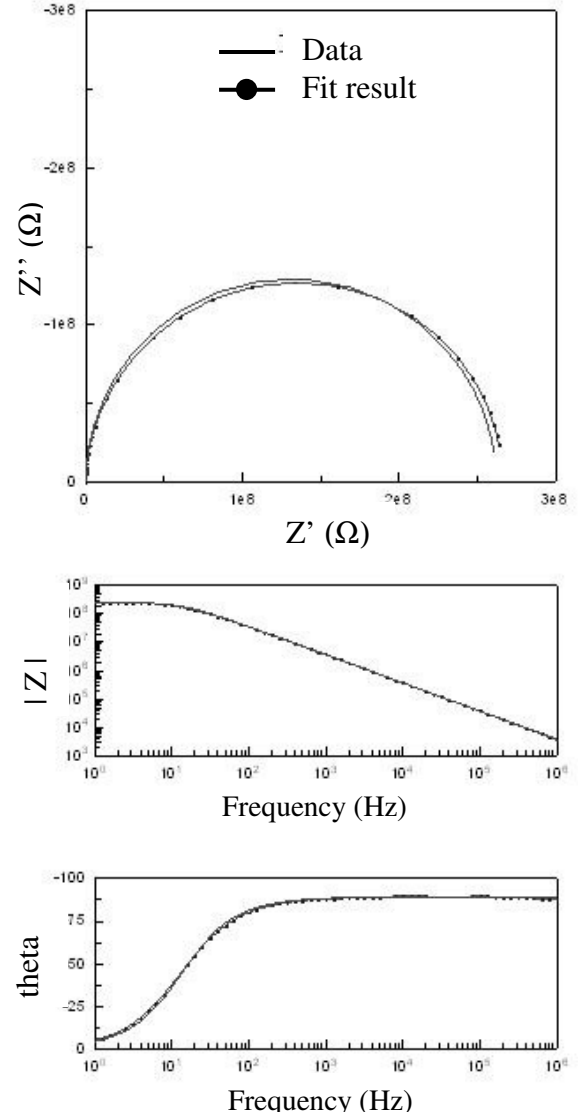


Figure 5: Equivalent circuit fit to the impedance data collected at 325 °C for a langatate single crystal along z-axis

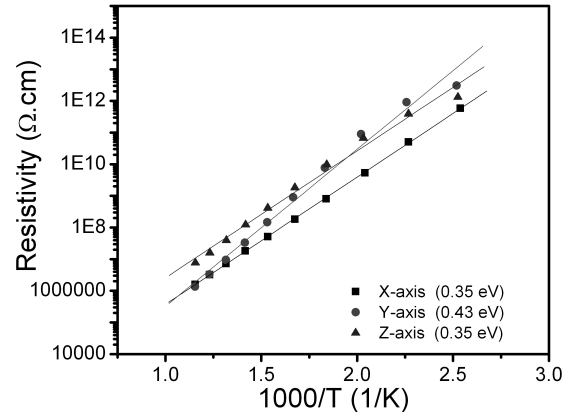


Figure 6: Arrhenius plots of resistivity and the activation energy of conduction calculated for x-, y- and z- directions of langatate single crystals.

4. SUMMARY:

- The langatate single crystals were successfully grown using a Czochralski technique up to 5 cm in diameter and 10 cm in length. Optimized growth conditions minimized the formation of striations and facilitated that, crystals grown of [001], [100] and [120] orientations were inclusion-free and colorless. The tight control of processing parameters provided a pathway to produce facet free crystals by controlling the solidification parameters at the liquid-solid interface.
- These high quality and defect free crystals have been used to determine the first order piezoelectric constants as a function of temperature. The high-field dielectric constant calculated from polarization loops was twice the value of the weak-field dielectric constant calculated from impedance measurements. A piezoelectric coefficient of 7pC/N was measured along the x-axis. This is significantly higher than quartz and may provide a pathway to engineer high temperature pressure sensors and other devices for wide range of applications.
- To assess the high temperature upper use temperature, the dielectric constant, loss tangent, and effective electromechanical coupling coefficient have been measured using different measurements techniques. Both x- and y-axes exhibited low temperature dependence of dielectric properties. The loss tangent was also low in all directions up to 600 °C. The combination of these properties and the absence of phase transformation demonstrated that langatate can be used as a pressure sensor at least up to 600 °C. Further experiments are in progress to assess the properties at even higher temperatures.
- The activation energies of conducting species along all axes were relatively similar (~0.35 – 0.40 eV) and did not show any change up to 600 °C. The exact mechanism for the conductivity and its relation to defect concentration are currently being investigated.

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